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Applicant's or agent's file reference 21620WO/1/	**IMPORTANT NOTIFICATION**
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Applicant DSM IP ASSETS B.V. et al	

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Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Peter WIMMER (Fax 338 8970)
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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03077434.3

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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R C van Dijk

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process for the preparation of an metal-organic compound comprising at least on imine ligand

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PROCESS FOR THE PREPARATION OF AN METAL-ORGANIC COMPOUND COMPRISING AT LEAST ONE IMINE LIGAND

The invention relates to a process for the preparation of an metal-organic compound comprising at least one imine ligand according to formula 1. Metal-organic compounds thus produced are typically used as precatalyst in the production of polyolefins. Imine ligands for these precatalyst can be guanidine, iminoimidazoline, ketimides or phosphinimine, the manufacturing of which is described in WO 2070569, US 6114481 and US 6063879 respectively.

The known production processes for phosphinimine comprising metal-organic compounds require at least two steps: (i) the synthesis of a N-trialkylsilyl substituted imine ligand, followed by (ii) contacting this ligand with an metal-organic precursor. However, in the one step process for the manufacturing of the imine ligand, as described in Z. Naturforschung. 29b, 328(1974) (the Staudinger reaction), azide chemistry is required. In this process, the most the frequently used azide is azidotrimethylsilane, which is highly toxic and readily hydrolysable, releasing the highly toxic and both temperature and shock sensitive hydrazoic acid. Therefore, mixtures containing (partially) hydrolysed trimethylsilylazide may explosively decompose.

A process for an azide-free preparation of imine ligands (i.c. phosphinimine) is described in Canadian patent application CA 2,261,518. However, this procedure encompasses two reaction steps starting from aminophosphoniumhalides. Another disadvantage of the method described in CA 2,261,518, is the use of harmful and costly reagents, such as *n*-butyllithium. Finally, in this procedure the imine ligand is substituted with trimethylsilylchloride, which is removed as such in a reaction of the imine ligand with the metal-organic precursor. Known production processes for guanidine-, ketimide- and iminoimidazoline comprising metal-organic compounds care described in WO 2070569 and US 6114481.They are carried out at low temperature and require in some cases a solvent change.

Disadvantage of the known less dangerous method is thus that at least two steps are required, when starting the process with an aminophosphoniumhalide. Purpose of the present invention is to provide a widely applicable method for the manufacturing of a metal-organic compound from an imine and a metal-organic precursor in one step.

This aim is achieved in that an imine ligand according to formula 1, or the HA adduct thereof, wherein HA represents an acid, of which H represents its proton and A its conjugate base, is contacted with a metal-organic reagent of formula 2 in the presence of at least 1, respectively 2 equivalents of base, wherein

$$Y=N-R \qquad \text{(formula 1)}$$

wherein Y is selected from a substituted carbon, nitrogen or phosphorous atom and R represents a protic or aprotic substituent, and:

$$M^V(L_1)_k(L_2)_l(L_3)_m(L_4)_nX \qquad \text{(formula 2)}$$

wherein:
M represents a group 4 or group 5 metal ion
V represents the valency of the metal ion, being 3, 4 or 5
L_1, L_2, L_3, and L_4 represent ligands on M and may be equal or different
X represents a group 17 halogen atom
k, l, m, n = 0, 1, 2, 3, 4 with k+l+m+n+1=V

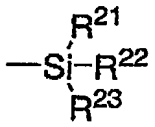
With the method of the invention a metal-organic compound, suitable as precatalyst in olefin polymerisation, is prepared in one step. An additional advantage of the method of the invention is, that during the process hardly any by-products are formed, so that further purification is not necessary (or very limited with respect to state of the art processes). The metal-organic compound prepared by the method of the invention has a higher purity than a metal-organic compound prepared via known production processes and can be used as such in olefin polymerisation processes. An additional advantage of the process of the invention is that the process can be carried out at room temperature, whereas the reaction of the N-trialkylsilyl substituted imine ligand with the metal-organic reagent has to be carried out at elevated temperatures.

The imine derivative or its HA adduct, as represented in formula 1, is substituted by an Y-and an R group. In the method of the invention, the Y group consists of a substituted carbon, nitrogen or phosphorous atom. If Y represents a substituted carbon atom, the number of substituents is 2. If Y represents a substituted nitrogen atom, the number of substituents is 1 and the number of substituents is 1or 3 if Y represents a phosphorous atom, depending on the valency of the phosphorous atom.

Substituents on carbon, nitrogen or phosphorous may be equal or different, optionally linked with each other, optionally having hetero atoms. Substituents may be protic or aprotic. A protic substituent is defined here as a substituent which has at least one group 15 or group 16 atom containing at least one proton.

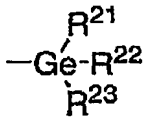
Examples of protic subsituents include C_1-C_{20} linear, branched or cyclic hydrocarbyl radicals, substituted with a group 15 or 16 atom bearing at least one hydrogen atom. Preferred protic substituents include phenolic radicals, pyrrolic radicals, indolic radicals, and imidazolic radicals.

The substituent is called aprotic if the substituent lacks a group containing a group 15 or group 16 atom bearing a proton. An unsubstituted aprotic hydrocarbyl radical can be a C_1–C_{20} linear, branched or cyclic radical, a hydrogen atom, a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

or a germanyl radical of the formula:



(formula 5)

wherein R^{2j} with j = 1 to 3 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, each substituent R^{2j} may be linked with another R^{2j} to form a ring system,

The substituent R can be H, or being equal as these for the substituent on Y.

Examples of imine ligands according to formula (1) thus include: guanidines, iminoimidazolines, phosphinimines, phenolimines, pyrroleimines, indoleimines and imidazoleimines.

R may be linked with Y, thus forming a ring system, optionally

comprising hetero atoms, or optionally comprising functional groups. Examples of ligands comprising such ring systems include: 8-hydroxyquinoline, 8-aminoquinoline, 8-phosphinoquinoline, 8-thioquinoline, 8-hydroxyquinaldine, 8-aminoquinaldine, 8-phosphinoquinaldine, 8-thioquinaldine and 7-azaindole or indazole.

In the process of the invention, HA represents an acid, of which H represents its proton and A its conjugate base. Examples of A are halogenides, such as fluoride, chloride, bromide, or iodide, sulfate, hydrogensulfate, phosphate, hydrogenphosphate, dihydrogenphosphate, carbonate, hydrogencarbonate, aromatic or aliphatic carboxylates, cyanide, tetrafluoroborate, (substituted) tetraphenylborates, fluorinated tetraarylborates, alkyl or aryl sulfonates.

With "at least 1, respectively 2 equivalens of a base", and lateron in the application "at least 3, respectively 4 equivalents of a base", is meant that at least 1, respectively 3 equivalents of a base are required when the imine ligand as such is used, but that at least 2, respectively 4 equivalents are required, in case the HA adduct of the imine ligand is used.

The metal-organic reagent used in the method of the invention is a reagent according to formula 2. In this formula L_1 to L_4 can independently be a monoanionic ligand or a group 17 halogen atom.

Examples of monoanionic ligands are: halides like a fluoride, chloride, bromide or iodide, (un)substituted aliphatic or aromatic hydrocarbyls, like C_1-C_{20} hydrocarbyl radicals, aryloxy or alkyloxy, cyclopentadienyls, indenyls, tetrahydroindenyls, fluorenyls, tetrahydrofluorenyls, and octahydrofluorenyls, amides, phosphides, sulfides, ketimides, guanidines, iminoimidazolines, phosphinimides, substituted imines, like (hetero)aryloxyimines, pyrroleimines, indoleimines, imidazoleimines or (hetero)aryloxides.

Preferred monoanionic ligands include: fluoride, chloride, bromide, iodide, C_1-C_{20} hydrocarbyl radicals, cyclopentadienyl, C_1-C_{20} hydrocarbyl substituted cyclopentadienyls, halogen substituted C_1-C_{20} hydrocarbyl substituted cyclopentadienyls, indenyl, C_1-C_{20} hydrocarbyl substituted indenyls, halogen substituted C_1-C_{20} hydrocarbyl substituted indenyls, fluorenyls, C_1-C_{20} hydrocarbyl substituted fluorenyls, halogen substituted C_1-C_{20} hydrocarbyl substituted fluorenyls, C_1-C_{45} substituted phosphinimides, C_1-C_{20} substituted ketimides, C_1-C_{30} substituted guanidines, C_1-C_{30} iminoimidazolines.

Most preferably monoanionic ligands are selected from fluoride, chloride, bromide, iodide, cyclopentadienyl, C_1-C_{20} hydrocarbyl (optionally containing

hetero- or group 17 halogen atoms), substituted cyclopentadienyls, indenyl, C_1-C_{20} hydrocarbyl substituted indenyls, and halogen substituted C_1-C_{20} hydrocarbyl substituted indenyls.

Depending on the valency of the metal of the metal-organic reagent, preferably at least one L_1, L_2, L_3, or L_4 represents a group 17 atom. If the valency of the metal V = 3, one or two ligands L may represent a group 17 atom. If V = 4, two or three ligands L may represent a group 17 atom. If V = 5, two to four ligands L may represent a group 17 atom. Preferred group 17 atom ligands are fluoride, chloride, bromide or iodide atoms. The most preferred group 17 atom ligand is chloride.

In the method of the invention an imine ligand or the HA adduct thereof according to formula 1, is contacted with a metal-organic reagent of formula 2 in the presence of at least 1, respectively 2, equivalents of a base. Examples of a base include, carboxylates (for example potassium acetate), fluorides, hydroxides, cyanides, amides and carbonates of Li, Na, K, Rb, Cs, ammonium and the group 2 metals Mg, Ca, & Ba, the alkali metal (Li, Na, K, Rb, Cs) phosphates and the phosphate esters (eg. $C_6H_5OP(O)(ONa)_2$ and related aryl and alkyl compounds) and their alkoxides and phenoxides, thallium hydroxide, alkylammonium hydroxides and fluorides. Some of these bases may be used in conjunction with a phase transfer reagent, such as for example tetraalkylammonium salts or crown ethers.

Also stronger bases may be applied, like carbanions such as hydrocarbanions of group 1, group 2, group 12 or group 13 elements. Also the metallic alkalimetals of group 1 may be applied as a base.

Preferred bases include amines, organolithium compounds, or organomagnesium compounds, alkali metals, group 1 hydrides or group 2 hydrides More preferred bases are mono-, di-, or tri-, alkylamines or aromatic amines, organolithium compounds, organomagnesium compound, sodium hydride or calciumhydride. Under aromatic amines is understood in this application compounds having a nitrogen atom in an aromatic ring system or mono-, di-, or triarylamines. Even more preferred bases are triethylamine, pyridine, tripropylamine, tributylamine, 1,4-diaza-bicyclo[2.2.2]octane, pyrrolidine or piperidine organolithium compounds, or organomagnesium compounds. Examples of organomagnesium compounds are: methylmagnesiumhalides, phenylmagnesiumhalides, benzylmagnesiumhalides, biphenylmagnesiumhalides, naphtylmagnesiumhalides, tolylmagnesiumhalides, xylylmagnesiumhalides, mesitylmagnesiumhalides, dimethylresorcinolmagnesiumhalides, N,N-dimethylanilinemagnesiumhalides,

dimethylmagnesium, diphenylmagnesium, dibenzylmagnesium, bis(biphenyl)magnesium, dinaphtylmagnesium, ditolylmagnesium, dixylylmagnesium, dimesitylmagnesium, bis(dimethylresorcinol)magnesium, bis(N,N-dimethylaniline)magnesium.

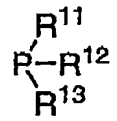
Examples of organolithium compounds are: methyllithium, phenyllithium, benzyllithium, biphenyllithium, naphtyllithium, dimethylresorcinollithium, N,N-dimethylanilinelithium.

In order to make a polyolefin by a borane or borate activatable metal-organic compound, the halide groups of the metal-organic compound from the process of the invention have to be alkylated or arylated. This can be done for example with an organolithium compound or an organo magnesium compound. Surprisingly it has been found that such alkylated or arylated metal-organic compound can also be prepared in one step by the process of the invention by carrying out the process in the presence of at least 3, respectively 4 equivalents of an organomagnesium compound or an organolithium compound as a base.

The reaction is preferably carried out in a solvent. Suitable solvents are solvents that do not react with the metal-organic reagent or the metal-organic compound formed in the process of the invention. Examples of suitable solvents include aromatic and aliphatic hydrocarbons, halogenated hydrocarbons, amides of the aliphatic carboxylic acids and primalry, secondary, or tertiary amines, DMSO, nitromethane, acetone, acetonitrile, benzonitrile, ethers, polyethers, cyclic ethers, lower aromatic and aliphatic ethers, esters, pyridine, alkylpyridines, cyclic and primary, or secondary amines, and mixtures thereof. Preferred solvents include aromatic or aliphatic hydrocarbons or mixtures thereof.

In a preferred embodiment of the method of the invention, R represents a hydrogen atom and Y is selected from the group consisting of:

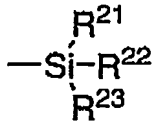
i) a phosphorus substituent according to the formula:



(formula 3)

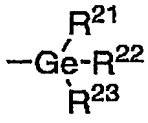
wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an

amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

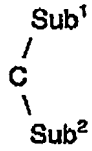
or a germanyl radical of the formula:



(formula 5)

wherein R^{2j}, with j=1-3, is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, each substituent R^{1j} or R^{2j} may be linked with another R^{1j} or R^{2j} respectively to form a ring system,

ii) a substituent according to formula 6:



(formula 6)

wherein each of Sub^1 and Sub^2 is independently selected from the group consisting of hydrocarbyl radicals having from 1 to 30 carbon atoms; silyl radicals, (substituted) amido radicals and (substituted) phosphido radicals, and wherein Sub^1 and Sub^2 may be linked with each other to form a ring system.

Preferably Sub^1 and Sub^2 are each independently selected from the group of C1-C20 hydrocarbyl radicals, or substituted amido radicals optionally linked by a bridging moiety.

The process of the invention can be carried out, by adding at least 1, respectively at least 2 equivalents of a base to a mixture of the imine ligand or its HA adduct and the metal-organic reagent thus forming a reaction mixture. The desired metal-organic compound is often formed instantaneously. Excess of a base may be applied without negative effects on the reaction product. If the reaction is exothermic, the reaction mixture may be cooled to a suitable temperature to control the reaction. If the reaction is slow, the reaction mixture may be heated in order to increase the reaction rate. During the reaction, a salt is formed. The reaction mixture as obtained by contacting an imine or its HA adduct may be used as precatalyst in a polyolefin polymerisation without an additional filtration step if the salt formed during the reaction is compatible with the polymerisation process. If a salt free metal-organic compound is required, the salt can be removed by using a filtration. Depending on the solubility of the metal-organic compound, the mixture may be heated and then filtered. An advantage of the present invention is that the filtrate may be used as such without further purification in a following process, such as an alkylation or arylation step or the polymerisation process. If desired, the metal-organic compound may be isolated by distillation of the solvent, by precipitation or by crystallisation from a suitable solvent.

The invention further relates to a process for the preparation of a polyolefin as described in claim 10. Such an olefin polymerisation can be carried out in solution, slurry or in the gas phase.

In a preferred embodiment of the olefin polymerisation the (alkylated) metal-organic compound is formed in situ. By in situ preparation is meant in this context, that the metal-organic compound is made and subsequently activated in or anywhere before the reactor of the polymerisation equipment by contacting an imine or its HA adduct with an metal-organic reagent in the presence of an olefin polymerisation compatible base. Examples of bases compatible with the olefin polymerisation process include amines, organomagnesium compound, organolithium reagents, organozinc reagents, organoaluminum reagents. More preferred bases are: aromatic amines, organomagnesium compound, organolithium reagents, organozinc reagents, organoaluminum reagents. Most preferred bases are N,N-dimethylaniline, diphenylmethylamine, triphenylamine, dibutylmagnesium, n-butyllithium, C_1-C_{20} dihydrocarbylzinc derivatives, diisobutylaluminium hydride, C_1-C_{20} trihydrocarbyl aluminiums, or aluminoxanes. In the case where aluminoxanes are applied as a base, the base can be the activator.

In the olefin polymerisation according to the invention, R preferably represents a

hydrogen atom and Y is preferably selected from the group consisting of:
i) a phosphorus substituent according to formula 3 of claim 2 or,:
ii) a substituent according to formula 6 of claim 2.
Advantages of the process of the invention are: higher yields, higher reaction rates and smaller amounts of by-products. The (alkylated) metal-organic compounds as obtained by the invented process can be used without further purification in the olefin polymerisation resulting in more active catalysts.

The invention will be elucidated with some non-limiting examples:

General part

Experiments were performed under a dry and oxygen-free nitrogen atmosphere using Schlenk-line techniques. ^{1}H-NMR, ^{13}C-NMR-spectra and ^{31}P-NMR-spectra were measured on a Bruker Avance 300 spectrometer. Diethyl ether and ligroin were distilled from sodium/potassium alloy; THF and toluene from potassium and sodium, respectively, all having benzophenone as indicator.
Tri-ethylamine was distilled from calciumhidoide before use.
Other starting materials were used as obtained.

Comparative experiment A

Synthesis of N-trimethylsilyltri-*tert*-butylphoshinimine

To neat tri-*tert*-butylphosphane (4.38 g, 21.7 mmol) was added azidotrimethylsilane (1. 00 mL, 0.87 g, 7.56 mmol). The mixture was heated to the temperature where the formation of nitrogen started (approximately 110°C). A white precipitate started to form. The remaining amount of azide (1.62 g, 14.1 mmol) was added portionwise in order to control the reaction. The product was distilled resulting in 4.20 g (66%) of N-trimethylsilyltri-*tert*-butylphoshinimine.

Preparation of (Cp)Ti(NP(t-Bu)$_3$)Cl$_2$ using CpTiCl$_3$ and N-trimethylsilyl-tri-tert-butylphoshinimine

To a solution of cyclopentadienyltitanium trichloride, CpTiCl$_3$ (0.430g, 1.96 mmol) in toluene (25 mL) was added solid N-trimethylsilyltri-*tert*-butylphoshinimine (0.566g, 1.96 mmol). The solution was heated to 60°C for 30 minutes and subsequently stirred overnight. The volatiles were removed in vacuo and the product was washed three times with ligroin. Drying of the yellow solid resulted in 0.63 g (81%). Overall yield

with respect to the phosphine: 53%.

Example I. One-step preparation of $(Cp)Ti(NP(t\text{-}Bu)_3)Cl_2$ from Tri-tert-butyl Aminophosphonium Chloride ($t\text{-}Bu_3PClNH_2$) and $CpTiCl_3$ using triethylamine as base

a. *Synthesis of $t\text{-}Bu_3PClNH_2$ at atmospheric pressure*

To a solution of tert-butylphosphane (4.06 g, 20.1 mmol) in ether (60 mL) was added hexachloroethane (4.76 g, 20.1 mmol). The mixture became heterogeneous. Acetonitrile (20 mL) was added to obtain a homogeneous solution. ^{31}P-NMR showed the oxidation to be complete. Ammonia gas was bubbled through at atmospheric pressure for 20 minutes. After 16 hours, the conversion appeared to be 71% according to ^{31}P-NMR. NH_3 was bubbled through again for 10 minutes. The reaction was complete after stirring for 3 days at room temperature and atmospheric pressure. The solvents were removed in vacuo resulting in 4.98 g (98%) of a white powder being characterized by ^1H-NMR and ^{31}P-NMR as tris(*tert*)butylaminophosphoniumchloride.

b. *One-step preparation of $(Cp)Ti(NP(t\text{-}Bu)_3)Cl_2$ from Tri-tert-butyl Aminophosphonium Chloride ($t\text{-}Bu_3PClNH_2$) and $CpTiCl_3$ using triethylamine as base.*

To a solution of commercially available $CpTiCl_3$ (0.55 g, 2.5 mmol) in toluene (20 mL) was added the aminophosphoniumchloride prepared under a (0.63 g, 2.5 mmol). To the almost clear solution was added an excess of triethylamine (2.5 mL, 18 mmol). The reaction mixture became more heterogeneous and the colour changed to orange. After stirring the reaction mixture overnight, the formed triethylammoniumchloride was filtered. The solvents from the filtrate were removed in vacuo. NMR analysis (^1H, ^{31}P and ^{13}C) showed $(Cp)Ti(NP(t\text{-}Bu)_3)Cl_2$ with no detectable amounts of by-product.

Example II. One-step preparation of $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Cl_2$ from Tri-tert-butyl Aminophosphonium Chloride ($t\text{-}Bu_3PClNH_2$) and $Cp(C_6F_5)TiCl_3$ using triethylamine as base

To a solution of $C_6F_5CpTiCl_3$ (1.00 g, 2.59 mmol) (obtained by the method described in *J. Organomet. Chem.*, 2000, 107 by Rausch et. al.) in toluene (60 mL) was added $t\text{-}Bu_3PClNH_2$ (0.68 g, 2.59 mmol). To the orange mixture was added triethylamine (1.0 mL, 7.2 mmol). A precipitate was formed immediately and NMR monitoring of the reaction mixture showed complete conversion to the desired

products, with no detectable amounts of by-product. The mixture was stirred for 3 days. The reaction mixture was filtered and the solvent and excess triethylamine were removed in vacuo resulting in 1.22 g (83%) $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Cl_2$. ^{31}P- and ^1H-NMR showed $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Cl_2$ with no detectable amounts of by-product.

Example III. One-step preparation of $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Me_2$ from Tri-tert-butyl Aminophosphonium Chloride (tBu_3PClNH_2) and $Cp(C_6F_5)TiCl_3$ using methylmagnesiumbromide as base

To an orange mixture of $C_6F_5CpTiCl_3$ (1.00 g, 2.59 mmol) and $t\text{-}Bu_3PClNH_2$ (0.68 g, 2.59 mmol) in toluene (60 mL) and THF (20mL) was added a MeMgBr solution in ether (3.0M, 4.0 mL, 12 mmol) at –20°C. The reaction mixture was stirred for 45 minutes and subsequently dried in vacuo. The residue was extracted with boiling ligroin (20 and 40 mL respectively). The solvents were removed in vacuo resulting in 1.33 g (98%) of $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Me_2$ with no detectable amounts of by-product.

Example IV. One-step preparation of $CpTi(NP(n\text{-}Bu)_3)Cl_2$ from Tri-n-butyl Aminophosphonium Bromide ($n\text{-}Bu_3PBrNH_2$) and $CpTiCl_3$ using triethylamine as base

a. *Synthesis of $n\text{-}Bu_3PBrNH_2$*

Tri-*n*-butylphosphane (20.2 g, 0.10 mol) was dissolved in acetonitrile (200mL). The solution was cooled to 0°C and bromine (16.2 g, 0.10 mol) was added in 10 minutes. An exothermic effect was observed. After 10 minutes, the cooling bath was removed. The bright yellow mixture was stirred for 2 hours after reaching room temperature. The mixture was again cooled to 0°C and ammonia was introduced. An exothermal reaction occurred. The temperature increase was controlled by the addition rate of the ammonia. The yellow slurry turns white after 15 minutes and ammonia was bubbled through for an additional 10 minutes. The acetonitrile was removed in vacuo and the residue was extracted with dichloromethane (2x150ml). The solution was decanted from the solids and the solvent was subsequently removed in vacuo resulting in a white solid. Yield: 28.2 g (95%) $n\text{-}Bu_3PBrNH_2$.

b. *One-step preparation of $CpTi(NP(n\text{-}Bu)_3)Cl_2$ from Tri-n-butyl Aminophosphonium Bromide ($n\text{-}Bu_3PBrNH_2$) and $CpTiCl_3$ using triethylamine as base*

$CpTiCl_3$ (2.21g, 10.1 mmols) and $n\text{-}Bu_3PNH_2Br$ (3.05g 10.2 mmols), were

dissolved in toluene (80mL). At room temperature triethylamine (4mL, 29 mmol) was added dropwise over a period of 10 minutes. The reaction mixture immediately became heterogeneous and the colour changed from orange to bright yellow. The mixture was stirred for 1 hour at room temperature (according to ^{31}P NMR the reaction was converted completely to the desired product). The ammoniumsalt was filtered off and washed once with 25 mL of toluene. The solvent was subsequently removed in vacuo leaving a viscous residue (product contaminated with small amounts of solvent). In order to obtain a solid product, the resulting residue was dissolved in 80 ml of hexanes and 25 mL of dichloromethane. Removing the solvent in vacuo yielded 3.4g of the product as a yellow solid (85%) being $CpTi(NP(n\text{-}Bu)_3)Cl_2$.

Example V. Synthesis of tris(N,N-dimethylamido)phosphoraneimido cyclopentadienyl titanium(IV) dichloride

To a cold solution (–60°C) of cyclopentadienyltitanium trichloride (0.50g, 2.28 mmol) in toluene (30 mL) was added N,N,N',N',N",N",N"',N"'-hexamethylphosphorimidic triamide (0.41 g, 2.3 mmol). The mixture was allowed to warm to room temperature. Then, triethylamine (1.0 mL, 7.2 mmol) was added. A precipitate formed directly after the addition of the triethylamine. ^{31}P-NMR reaction monitoring showed that the desired product was formed without any detectable amount of by-product. The reaction mixture was filtered in order to remove the triethylammonium chloride. The solvents were removed in vacuo and the residue was crystallised from toluene to give 0.73 g (yield: 89%) of a yellow crystalline product, which was characterized by ^{1}H- and ^{31}P-NMR to be tris(N,N-dimethylamido)phosphoraneimido cyclopentadienyl titanium(IV) dichloride.

Example VI. Synthesis of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride

To a suspension of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline (1.50 g, 5.0 mmol) (prepared according to the procedure by L.Toldy et al, US Patent 4,284,642), and cyclopentadienyltitanium trichloride (1.10 g, 5 mmol) in toluene (80 mL) was added triethylamine (1.0 mL, 7.2 mmol) at ambient temperature. After stirring for 1 hour, the suspension was heated to reflux, then filtered hot. Cooling to ambient temperature gave orange crystals, which were filtered, washed with cold toluene and dried (1.36 g, 57% yield). Partial evaporation of the mother liquor and cooling to –20 °C

afforded another 0.90 g (38%). Total yield of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride was 95%.

Example VII. Synthesis of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl

To a suspension of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline (5.86 g, 20.0 mmol) and cyclopentadienyltitanium trichloride (4.39 g, 20.0 mmol) in toluene (200 mL) was added triethylamine (2.53 g, 25 mmol) at ambient temperature. After stirring for 1 hour at ambient temperature, the thick yellow-orange suspension was heated to reflux and filtered hot. The yellow residue was extracted with boiling toluene portions of 10 mL 4 times (leaving a grey-white residue). The combined orange filtrates (separating yellow-orange crystals upon cooling) were cooled to 0°C. Methyl magnesium bromide (14 mL of a 3.0 M solution in diethyl ether, 44 mmol) was added in 10 minutes. The orange suspension turned yellow gradually. The mixture was stirred overnight, then evaporated to dryness. The residue was extracted with boiling ligroin (200 mL) and the resulting suspension was filtered hot. Cooling to approx. -20°C afforded yellow crystals, which were filtered and washed with cold ligroin to give 2.8 g (32% yield) of NMR pure product. From the partially evaporated mother liquor and 2nd ligroin extract, a 2nd fraction of pure product was obtained (1.0 g, 11%). Total yield of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl was 43%.

Example VIII. Synthesis of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl using methylmagnesium bromide as base.

To a suspension of 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline (2.93 g, 10.0 mmol) and cyclopentadienyltitanium trichloride (2.19 g, 10.0 mmol) in toluene (100 mL) was added methylmagnesiumbromide (11 mL of a 3.0 M solution in diethyl ether, 33 mmol) at -80°C during 10 minutes. The mixture was allowed to warm to ambient temperature to give a yellow suspension. THF (30 mL) was added, and the mixture was stirred for 15 hours. The light yellow suspension was evaporated to dryness. The residue was extracted with boiling ligroin (100 mL). The resulting suspension was filtered hot. The cake was extracted further with hot ligroin (Three times with 60 mL until the filtrate became colourless). The combined yellow filtrates were partially evaporated under reduced pressure to 50 mL. Cooling to approx. 4°C afforded yellow crystals, which were filtered and washed with cold ligroin to give 2.05 g

(47% yield) of NMR pure 1,3-bis(2,6-dimethylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl.

Example IX. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride

a. *Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline*

To a mixture of 2,6-diisopropylaniline (260 g, 1.47 mol) in ethanol (1200 mL) was slowly added glyoxal (108.5 g of a 40 w-% in water solution, 0.75 mol). The solution turned intensely red, then intensely yellow. The mixture was heated to reflux overnight. Cooling to 4 degrees resulted in crystallisation of yellow material, which was filtered and washed with cold ethanol until filtrate became bright yellow (instead of brown). The bright yellow powder was dried (202.6 g, 72%). This diimine (100 g, 0.27 mol) was dissolved in ethanol (1000 mL). The mixture was cooled to 0°C. Sodium borohydride (102.1 g, 2.7 mol) was added in portions during 1 hour. The mixture was allowed to warm to room temperature, then stirred 1 hour. The mixture was heated to reflux gently (gas evolution!) and heated to reflux for 1 hour. After cooling, the mixture was admixed with water (2L), and the suspension filtered. The yellow precipitate was dried (100.1 g, 98%).

57 g (0.15 mol) of the diamine was dissolved in toluene (250 mL) and heated to reflux. A solution of cyanogen bromide (19.1 g, 0.18 mol) in toluene (100 mL) was added during the course of ~1 hour, resulting in formation of a grey precipitate in an orange-red solution. After stirring at reflux for 1 hour, the mixture was cooled. The precipitate was filtered, washed with toluene and ligroin (to give 47.1 g yellow light powder). This powder was dissolved in water/ethanol 400/500 mL, and 10.0 M NaOH in water was added until strongly basic (pH>10). The precipitate was filtered and washed with water, then dried to give 37.3 g (61.4% yield) of near pure product. The iminoimidazoline can be crystallized to give pure material as colourless crystals from boiling ligroin (270 mL) and filtering hot to remove some insoluble material (recovery 67%).

b. *Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride*

To a suspension of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline (1.02 g, 2.5 mmol) and cyclopentadienyltitanium trichloride (0.55 g, 2.5 mmol) in toluene (20 mL) was added triethylamine (0.4 mL, 4.0 mmol) at ambient temperature. After stirring for 2 hours, the thick yellow-orange suspension was filtered, and the filtrate

evaporated to dryness to afford 1.31 g (89% yield) of NMR-pure 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyltitanium dichloride.

c. *Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride* (reversed addition)

The same result as under b. was obtained when cyclopentadienyltitanium trichloride and triethylamine were admixed in toluene, and then ligand was added.

d. *Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride*

To a suspension of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline (2.03 g, 5.0 mmol) and cyclopentadienyltitanium trichloride (1.10 g, 5.0 mmol) in toluene (30 mL) was added triethylamine (0.8 mL, 5,7 mmol) at ambient temperature. After stirring for 1 hour, the thick yellow-orange suspension was diluted with toluene (50 mL) and ligroin (120 mL). The suspension was heated to reflux and filtered hot. Cooling to approx. 4°C afforded yellow crystals, which were filtered and washed with cold ligroin to give 1.34 g (46% yield) of NMR pure 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dichloride.

Example X. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl

To a suspension of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline (2.06 g, 5.0 mmol) and cyclopentadienyltitanium trichloride (1.10 g, 5.0 mmol) in toluene (40 mL) was added triethylamine (0.8 mL, 5.7 mmol) at ambient temperature. After stirring for 2 hours, the thick yellow-orange suspension was filtered, and the residue washed with toluene. The clear and orange filtrate was partially evaporated (~10 mL solvent removed). After cooling to –78 °C (dry ice/acetone), methyl magnesium bromide solution (3.3 mL of a 3M solution in diethyl ether, 10.0 mmol) was added. The temperature of the mixture was allowed to rise to ambient temperature and the mixture was stirred overnight. The yellow suspension was evaporated to dryness. The residue was extracted with boiling ligroin (80 mL) and the resulting suspension was filtered hot. Evaporation to ~30 mL and cooling to approx. 4°C afforded yellow crystals, which were filtered and washed with cold ligroin to give 1.38 g (51% yield) of NMR pure product. From the partially evaporated mother liquor, a 2nd fraction of pure 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl was obtained (0.58 g, 19%). Total yield of 1,3-bis(2,6-diisopropylphenyl)-iminoimidazoline cyclopentadienyl titanium dimethyl: 70%.

CLAIMS

1. A process for the preparation of a metal-organic compound, comprising at least one imine ligand, characterized in that an imine ligand according to formula 1 or the HA adduct thereof, wherein HA represents an acid, of which H represents its proton and A its conjugate base, is contacted with a metal-organic reagent of formula 2 in the presence of at least 1, respectively at least 2 equivalents of a base, with

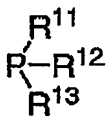
$$Y{=}N{-}R \qquad \text{as formula 1,}$$

wherein Y is selected from a substituted carbon, nitrogen, or phosphorous atom and R represents a substituent, and with

$$M^{V}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX \qquad \text{as formula 2,}$$

wherein:
M represents a group 4 or group 5 metal ion
V represents the valency of the metal ion, being 3, 4 or 5
L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different, X represents a group 17 halogen atom,
k, l, m, n = 0, 1, 2, 3, 4 with k+l+m+n+1=V.

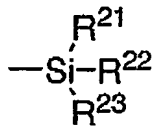
2. A process according to claim 1 wherein R represents a hydrogen atom and wherein Y is selected from the group consisting of:
I) a phosphorus substituent defined by the formula:



(formula 3)

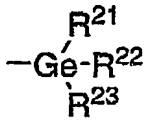
wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10}

aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



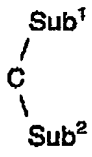
(formula 4)

or a germanyl radical of the formula:



(formula 5)

wherein R^{2j} is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals,
each substituent R^{1j} or R^{2j} may be linked with another R^1 or R^2 to form a ring system,
ii) a substituent defined by formula 6:



(formula 6)

wherein each of Sub^1 and Sub^2 is independently selected from the group consisting of hydrocarbyl radicals having from 1 to 30 carbon atoms; silyl radicals, (substituted) amido radicals and (substituted) phosphido radicals, and wherein Sub^1 and Sub^2 may be linked with each other to form a ring system

3. A process according to claim 1 or 2 wherein the base is an amine, a group 1, 2, 12, 13 hydrocarbanion or a metal or metalloid hydride.
4. A process according to claim 3 wherein the base is an amine, a group 1 hydride or a group 2 hydride, an organomagnesium- or an organolithium compound.
5. A process according to claim 4 wherein the base is a dialkylamine, a

trialkylamine, a diarylamine or a triarylamine, an organomagnesium- or an organolithium compound.

6. A process according to claim 5 wherein the base is triethylamine, pyridine, tripropylamine, tributylamine, 1,4-diaza-bicyclo[2.2.2]octane, pyrrolidine or piperidine, an organomagnesium- or an organolithium compound.

7. A process according to claim 1-6, carried out in the presence of at least 3 respectively 4 equivalents of an organolithium- or an organomagnesium compound.

8. A process according to claim 1-6 wherein the reaction is carried out in an aprotic solvent.

9. A process according to claim 8, wherein the solvent is the base.

10. Process for the preparation of a polyolefin in the presence of an activator, characterized in that the process is carried out in the presence of a metal-organic compound comprising at least one imine ligand according to formula 1 of claim 1, obtained by a process wherein an imine, or the HA adduct thereof, wherein HA represents an acid, of which H represents its proton and A its conjugate base, is contacted with a metal-organic reagent of formula 2 of claim 1 in the presence of at least 1 equivalent, respectively at least 2 equivalents of a base.

11. A process according to claim 10 wherein R represents a hydrogen atom and wherein Y is selected from the group consisting of:
a phosphorus substituent according to formula 3 or a substituent according to formula 6.

12. A process according to claim 10 or 11, carried out in the presence of at least 3, respectively at least 4 equivalents of an organomagnesium- or an organolithium compound, as the base.

13. Process according to any of claims 10-12, wherein the metal-organic compound is formed in situ.

ABSTRACT

The invention relates to a process for the preparation of a metal-organic compound, comprising at least one imine ligand, characterized in that an imine ligand according to formula 1 or the HA adduct thereof, wherein HA represents an acid, of which H represents its proton and A its conjugate base, is contacted with a metal-organic reagent of formula 2 in the presence of at least 1, respectively at least 2 equivalents of a base, with

$$Y{=}N{-}R \qquad \text{as formula 1,}$$

wherein Y is selected from a substituted carbon, nitrogen, or phosphorous atom and R represents a substituent, and with

$$M^{V}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX \qquad \text{as formula 2,}$$

wherein:
M represents a group 4 or group 5 metal ion
V represents the valency of the metal ion, being 3, 4 or 5
L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different X represents a group 17 halogen atom,
k, l, m, n = 0, 1, 2, 3, 4 with k+l+m+n+1=V.

The invention further relates to a process for the preparation of a polyolefin in the presence of the compound prepared according to the process of the invention.